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A Multi-Tracer Push-Pull Diagnostic Test for Assessing the Contributions of Volatilization and Biodegradation During In Situ Air Sparging

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This paper describes the development and application of a diagnostic tool for local measurements of mass transfer during operation of an IAS system. The diagnostic test involves injecting a solution containing multile tracer compounds through a monitoring well, piezometer, or drive point into the target treatment zone. The injected solution is initially deoxygenated and can contain: a) a non-degradable, non-volatile conservative tracer, b) one or more non-degradable, volatile chemicals, and c) a biologically degradable, non-volatile compound. After a predetermined hold time, an excess quantity of groundwater is extracted from the same injection point and then changes in the concentrations of the tracer compounds are measured. Volatilization and oxygen consumption rates are then estimated from mass balances on the tracer components. This approach is different from other IAS monitoring options in that the measurements can be made without requiring pre-IAS data and results and can be obtained relatively quickly. Furthermore, in principle, the approach is capable of assessing both the rate of oxygen transfer to the aquifer and the rate of volatilization from the aquifer.

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A Multi-Tracer Push-Pull Diagnostic Test for Assessing the Contributions of Volatilization and Biodegradation during In Situ Air Sparging

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1.0 INTRODUCTION

In-situ air sparging (IAS) generally involves the injection of air into a contaminated aquifer below the zone of contamination (Johnson et al., 1993; Marley and Bruell, 1995). The air injection promotes both volatilization and biodegradation of aerobically biodegradable compounds. The rate and extent of these processes varies, and is likely controlled by chemical properties, aquifer characteristics, the contaminant distribution, system design, and operating conditions. The IAS systems found at service station sites are frequently coupled with soil vapor extraction (SVE) systems in order to capture the liberated contaminant vapors and to minimize the potential for adverse vapor migration. At other remote sites, or at sites where the residence time of vapors in the vadose zone may be long enough to achieve sufficient biodegradation, an SVE system might not be necessary.

IAS has gained widespread use due to its apparent simplicity. Typical designs involve vertical wells, compressors, and timer-actuated solenoids when systems are operated in a pulsed mode. The number of wells and size of each compressor are chosen empirically, with there being a range of design and operation philosophies amongst practitioners (Johnson et al., 1993, Leeson et al., 1999; Marley and Bruell, 1995). For example, some prefer to operate air sparging systems in a "biosparging" mode, where lower air flow rates are used (<10 ft^3/min per vertical well) in an effort to maximize aerobic biodegradation, minimize volatilization, and avoid the need for an SVE system.

While IAS systems have been used to successfully achieve closure at many sites, the overall performance has been variable (Bass and Brown, 1995). This is likely a reflection of several factors, including: a) the unpredictability of saturated zone air distributions in many hydrogeologic settings, b) the range of empirical design and operating approaches, and c) the limited performance monitoring and lack of system optimization that occurs at most sites.

Monitoring plans for IAS systems are frequently minimal, and are primarily intended to satisfy regulatory compliance requirements. When an SVE system is being operated, off-gas contaminant concentrations and flow rates are generally monitored; otherwise, performance monitoring is most often restricted to quarterly (or less frequent) groundwater monitoring. Performance is then judged by changes in the dissolved concentrations over periods of months to years.

Of the conventional monitoring approaches, SVE off-gas monitoring provides the only real-time measure of remediation performance. Even then, it is an integrated measurement lacking in spatial resolution and the data reflects removal of contaminants from both above and below the groundwater table. Furthermore, this data is not available from those sites operated without SVE systems.

The implications of these observations are significant with respect to the operation, monitoring, and optimization of IAS systems. First, when groundwater sampling and analysis is the only performance monitoring option (or when an SVE system is present, but off-gas concentrations fall below measurable levels), then conclusions regarding performance can only be drawn after collecting data over fairly long time intervals (months to years). Second, the time period for this performance measurement is comparable to the overall remediation time frame, so optimization is impracticable. Third, without some real-time measure of performance, it is difficult to assess when to turn an IAS system off, and consequently: a) many systems may be operating longer than is necessary, and b) many systems may be terminated prior to achieving their full potential for remediation.

Thus, there is a need to develop procedures, or "diagnostic tools" that are capable of more real-time IAS performance assessment. While diagnostic tools are not common in the remediation field, a good example is the bioventing respirometry test described by Hinchee and Ong (1992). There, declines in soil gas oxygen concentrations are monitored with time following the cessation of steady air injection, and the rate of decline is used to assess the aerobic biodegradation rate. Respirometry tests typically require 2 to 4 days to complete and are performed periodically (at a frequency of 3 to 12 months). Similar types of tests were considered in this work (i.e., monitoring dissolved oxygen level declines with time after cessation of air injection), but this route was not pursued because IAS introduces a significant mass of oxygen in the form of trapped gas in the aquifer, and it is difficult to account for this unknown, but significant oxygen mass when interpreting dissolved oxygen changes with time. Furthermore, stratified gas pockets at some sites can continue to off-gas for hours to days following cessation of gas injection and this further complicates the application and interpretation of a respirometry-type IAS test.

This paper describes the development and application of a diagnostic tool for local measurements of mass transfer during operation of an IAS system. The diagnostic test involves injecting a solution containing multiple tracer compounds through a monitoring well, piezometer, or drive point into the

target treatment zone. The injected solution is initially deoxygenated and can contain: a) a non-degradable, non-volatile conservative tracer, b) one or more non-degradable, volatile chemicals, and c) a biologically degradable, non-volatile compound. After some predetermined hold time, an excess quantity of groundwater is extracted from the same injection point and then changes in the concentrations of the tracer compounds are measured. Volatilization and oxygen consumption rates are then estimated from mass balances on the tracer components. This approach is different from other IAS monitoring options in that measurements can be made without requiring pre-IAS data and results can be obtained relatively quickly. Furthermore, in principle, the approach is capable of assessing both the rate of oxygen transfer to the aquifer and the rate of volatilization from the aquifer. This tool is complementary to the diagnostic mass transfer test that uses tracer gas delivery described by Bruce et al. (2000) and Amerson (1997). There are similarities between this diagnostic test and the push-pull test described by Istok et al. (1997) and Schroth et al. (1998) for assessing microbial respiration during natural attenuation. The mechanics of both tests are similar; however, the multi-tracer solution used and the data reduction approaches are different. These differences result from the differences in the objectives of each test (e.g., assessing anaerobic and aerobic activity versus assessing aerobic activity and volatilization as with the diagnostic test described in this paper), as well as the differences in conditions in the aquifer during both tests (e.g., natural conditions versus air injection conditions).

2.0 OVERVIEW OF THE MULTI-TRACER PUSH-PULL DIAGNOSTIC TEST

Use of the multi-tracer push-pull diagnostic tool is illustrated in Figure 1. During IAS operation, a solution containing multiple tracer compounds is injected through a monitoring well, piezometer, or drive point and into the desired zone of treatment as well as a "background" point. The injected solution is initially deoxygenated and contains: a) a non-degradable, non-volatile conservative tracer, b) a non-degradable, volatile conservative tracer, c) a readily aerobically biodegradable, non-volatile compound, and d) a visible dye.

After some period of time, an excess quantity of groundwater is extracted from the subsurface and concentrations of the tracer compounds are determined. Volatilization and biodegradation rates are then estimated from mass balances on the tracer compounds, as well as the results from background points that lie in areas not impacted by the IAS system.

As mentioned earlier, the diagnostic test can be used to assess performance at a range of scales; therefore, the user selects an injection volume consistent with their goals. To estimate this volume, one can use the following calculation:

$$V_{inject} = \frac{4 \pi \theta R_{test}^3}{3} + V_{well} \quad (1)$$

Where: V_{inject} =multi-tracer injection volume (mL); $\pi = 3.14$; R_{test} = radial distance about injection point desired to be assessed (cm); θ = water content (approximately equal to the porosity) (mL-pores/mL-soil); V_{well} = volume of groundwater in the well and borehole that must be displaced (mL).

Ideally, $V_{well} << V_{inject}$ to minimize well dilution effects. For example, the results presented below from the field site application are for V_{inject} = 1,000 mL and V_{well} <10 mL, which corresponds to assessing performance within a radial distance of approximately 9 cm about the injection point. With respect to extracted volumes, experience suggests that extracting four to five times the injected volume provides reasonable recovery (typically >80%) of the conservative tracer.

3.0 DATA REDUCTION

Data from the push-pull test is evaluated to calculate a volatilization rate and an oxygen utilization rate. The oxygen utilization rate can then be converted into a biodegradation rate as described later in this section. Required data include the initial concentrations of the tracer compounds in the injection solution (C_{inject} [mg/L]), the volume of the mixed tracer solution injected into the subsurface (V_{inject} [L]), the dissolved oxygen concentration in the groundwater from the point of interest (DO [mg/L]), tracer concentrations in the extracted groundwater ($C_{recovered}$ [mg/L] and $C_{recovered\text{-}background}$ [mg/L]), the volume extracted ($V_{recovered}$ [L]), and the time the solution was held in situ ($T_{in\ situ}$ [d]).

Measured tracer concentrations from extracted groundwater samples first need to be adjusted for losses by other mechanisms (e.g., incomplete recovery due to groundwater movement away from the injection point). Adjusted concentrations are calculated by dividing all other tracer concentrations by the fraction of conservative tracer (e.g. Br^-) recovered. For example, to adjust the recovered concentration of acetate:

$$C^{*}_{Ac\ recovered} = \frac{C_{Ac\ recovered}}{C_{Br\ recovered} / C_{Br\ injected}}$$

Typical conservative tracer recoveries for the tests described later are 0.8 to 1.0, but are sometimes as low as 0.5.

Calculation of oxygen transfer and aerobic biodegradation rates derive from a mass balance on the aerobically biodegradable compound. First, the mass of biodegradable compound recovered is subtracted from the mass injected into the system and then it is corrected for the mass lost at a background monitoring point.

$$M_{lost} = C_{inject}\ V_{inject} - \left(C_{inject}\ V_{inject} - C^{*}_{recovered-background}\ V_{recovered-background}\right) - C^{*}_{recovered}\ V_{recovered} \quad (2)$$

Where C_{inject} = concentration of biodegradable tracer in injected mixed tracer solution (mg/L); V_{inject} = volume of mixed tracer solution injected into the monitoring location (L); $C^{*}_{recovered\text{-}background}$ = concentration in recovered solution at background point, after adjustment for conservative tracer recovery at that point (mg/L); $V_{recovered\text{-}background}$ = volume of solution recovered at background point (L); $C^{*}_{recovered}$ = concentration of biodegradable tracer in recovered solution at point of interest, after adjustment for conservative tracer recovery at that point (mg/L); $V_{recovered}$ = volume of solution recovered at point of interest (L).

The mass of biodegradable compound lost can then be converted to an equivalent mass of oxygen consumed, $M_{oxygen\text{-}consumed}$, assuming complete mineralization. For example, for acetate (CH_3COO^-):

$$CH_3COO^- + H^+ + 2O_2 + 8e^- \rightarrow 2H_2O + 2CO_2 \quad (3)$$

Therefore, 2 moles of oxygen are required to degrade 1 mole of acetate or 64 g of oxygen are required for degradation of every 59 g of acetate (1.08 g O_2/g acetate). A simple conversion is then required to get the mass of oxygen consumed ($M_{oxygen\ consumed}$ [g]):

$$M_{oxygen\ consumed} = M_{Ac\ lost} \times \frac{1.08\ g\ O_2}{g\ acetate} \quad (4)$$

Where M_{Ac} is the mass of acetate lost (g) as calculated by equation (2). An oxygen utilization rate $R_{oxygenation}$ (mg-O_2/L-water/d) can then be calculated by dividing $M_{oxygen\text{-}consumed}$ by the in situ hold time ($T_{in\ situ}$ [d]) and the tracer injection volume:

$$R_{oxygenation} = \frac{M_{oxygen\ consumed}}{T_{in\ situ}\ V_{inject}} \tag{5}$$

This results in an oxygenation rate that can be reported in units of mg-O_2/L-water/d. It should be noted that this manipulation might overestimate the actual oxygen mass transfer rate because it assumes that all of the biodegradable compound lost was completely mineralized. It might also underestimate the oxygenation rate because other oxygen demands are being neglected. This oxygenation rate can also be expressed as a potential hydrocarbon aerobic biodegradation rate (mg-hydrocarbon/L-water/d) by dividing the result by an approximate stoichiometric conversion factor for typical petroleum hydrocarbons of interest (approximately 3 mg-O_2/mg-hydrocarbon degraded [Leeson and Hinchee, 1996]). Hydrocarbon biodegradation rates can also be converted to zero-order rates expressed as (mg-contaminant/kg-soil/d) by dividing by the soil bulk density (approximately 1.7 kg-soil/L-soil) and multiplying by the volumetric moisture content (approximately 0.3 L-water/L-soil).

Calculation of a volatilization rate also derives from a mass balance similar to that discussed above in Equation (2) (using volatile tracer concentrations in place of biodegradable tracer concentrations). In this case, however, we choose to express the volatilization rate, $R_{volatilization}$, as a percent reduction per time (% loss/d), and this is obtained by:

$$R_{volatilization} = \frac{M_{lost}}{T_{in\ situ}\ M_{initial}} \times 100 \tag{6}$$

Where $T_{in\ situ}$ denotes the in situ hold time (d); M_{lost} is the mass of volatile, non-biodegradable tracer lost after correcting for background losses (g); and $M_{initial}$ is the initial volatile tracer mass (g). It is expressed in this way as $R_{volatilization}$ should be regarded as a relative (and not absolute) measure of volatilization rates. Increases or decreases in this quantity with changes in IAS process conditions should correlate with increases and decreases in actual volatilization rates for contaminants of interest.

5.0 DEVELOPMENT OF THE PUSH-PULL DIAGNOSTIC TEST PROTOCOL

Diagnostic test development involved a sequence of steps, including: a) tracer selection, b) protocol and analyses methods development, c) protocol evaluation in a three-dimensional laboratory-scale aquifer physical model, and finally, d) field evaluation. Complete details of the development studies can be found in Amerson (1997). The key points of steps (a) through (c) are summarized below, followed by a presentation of results from step (d).

With respect to the selection and analyses of tracer compounds:

1) Non-degradable, non-volatile conservative tracer: Most often this will be a non-nutrient salt that is easily analyzed with an ion-specific electrode or by ion chromatography. It is important to use initial concentrations that are detectable at a minimum 10X dilution, but also to ensure that the initial concentration is not so high as to induce significant vertical density gradients in the aquifer (e.g. initial salt concentrations should be <100 mg/L). In this work, bromide (Br-) was selected because it is typically found only in trace quantities in groundwater systems and is easily measured, either with an ion chromatograph, a bromide-specific electrode, or a spectrophotometer (colorimetric assay).

   In this work, stock solutions of bromide were prepared using the KBr salt, the injection concentration was typically approximately 50 mg/L, and the analyses were performed using a Dionex DX500 Ion Chromatograph equipped with an Ionpac® AS12A analytical column, Ionpac®12A guard column and electrochemical and conductivity detectors. Using this method, concentrations above 1 mg/L are easily quantified.

2) Biodegradable, non-volatile tracer compound: This compound should be readily biodegradable aerobically, and should have the potential to degrade much faster aerobically than via any other pathway during the time of the test. As above, it is important to use initial concentrations that are detectable at a minimum 10X dilution, but also to ensure that the initial concentration is not so high as to induce significant vertical density gradients in the aquifer (e.g. initial concentrations should be <100 mg/L). In this work, acetate (Ac^-) was selected because it is readily used as an energy source (electron donor) by a wide range of microbial organisms under aerobic growth conditions. Acetate was chosen over other degradable tracers such as ethanol, because it is not a component of petroleum fuel mixtures.

   In this work, stock Ac^- solutions were prepared using the NaAc salt, the injection concentration was typically approximately 50 mg/L, and the analyses were performed using the same ion chromatograph set-up described above for bromide analysis. Using this method, concentrations above 1 mg/L are easily quantified.

3) Volatile, non-degradable tracer compound: This compound should be chemically stable for the duration of the test, but should be capable of being volatilized. Theory (Johnson, 1998) suggests that results of this test should be insensitive to specific values of chemical parameters related to volatilization (e.g., vapor pressure and Henry's Law

Constant) as volatilization is expected to be diffusion-limited (not partitioning-limited). In this work, sulfur hexafluoride (SF_6) was chosen because it is sparingly soluble in water and it is easily detected in the low part per thousand (ppt_v) range with the use of a gas chromatograph (GC) equipped with an electron capture detector (ECD).

As SF_6 is a gas at normal ambient temperatures and pressures, SF_6 was allowed to diffuse into the solution by using a peristaltic pump to circulate the headspace containing 10 ppm_v of SF_6 above the Br^-/Ac^- solution. A glass bottle containing the Br^-/Ac^- solution was sealed using a No. 5 rubber stopper and 1 mL of 1,000 ppm_v SF_6 in N_2 was introduced to the resulting 100 mL headspace to produce the desired concentration of 10 ppm_v. The headspace was allowed to circulate for 30 to 40 min after the SF_6 was introduced.

Dissolved SF_6 concentrations were determined by a method that takes advantage of the high Henry's Law Constant: a) a sample of water was introduced into a sealed container and allowed to equilibrate with of headspace, b) a headspace gas sample was then analyzed for SF_6, and c) the dissolved SF_6 concentration was determined from a mass balance using the known water and headspace volumes and assuming that most of the SF_6 has partitioned into the headspace as shown.

Vapor samples were analyzed for SF_6 using a Lagus Applied Technologies Autotrac tracer gas analyzer equipped with an ECD. The Autotrac has a self-calibration feature that allows it to make a one-point calibration based on a 4.92 ppb_v standard.

4) Visible dye: This tracer is used to visually assess when the volume of solution recovered from the aquifer is sufficient to have recovered a significant fraction of the injected solution. The dye can be degradable, provided that the degradation rate is slow compared to the test duration. Fluorescein was used as it produces a bright green color at low concentrations; it is also easily measured by spectrophotometry and therefore concentrations can be quantified if desired (not done in this work).

Controlled experiments were conducted in order to evaluate and refine the proposed experimental procedure prior to field application. Experiments were conducted in a 4-ft tall × 4-ft wide × 8-ft long physical model. Using ports placed at the ends and sides of the tank, groundwater flow across the tank can be induced and air can be injected at the center of the tank near the bottom. The physical model was filled with unwashed fill sand, except 6-inches from each end, where a more permeable ABC composite was placed to better distribute water when groundwater flows were being simulated. Stainless steel tubing (1/8-inch inner diameter [ID]) sampling points were placed throughout the tank at sampling depths ranging from 1 to 3 ft below the upper soil surface.

Controlled experiments were conducted to assess the effects of in situ hold time and cumulative volume recovered on the test results, and to determine if the test was sufficiently sensitive to identify areas affected and unaffected by air sparging. In general, 800 to 900 mL of the tracer solution was

injected, and hold times of 5 min, 1 h, 4 h, 24 h, and 48 h were studied. Eight to ten L of water was extracted in 1-L increments, and points affected and unaffected (as measured by dissolved oxygen changes) were tested in these experiments.

First it was discovered that >90% recovery of the bromide tracer occurred after a recovery volume approximately equal to 4 times the injection volume. Acetate recovery was similar to bromide recovery for the 5-min in situ hold time tests, and then declined for longer in situ hold times. Complete disappearance of the acetate would occur by approximately 48 h in situ. Recovery of the SF_6 was generally <50%, and did not exhibit any clear dependence on in situ hold time.

Figure 2 presents representative results from this work. Here, recoveries from an affected (increased dissolved oxygen to >6 mg/L) and an unaffected (maintained <1 mg/L dissolved oxygen) monitoring point are presented. The acetate and SF_6 recoveries presented have been adjusted for bromide recovery. As can be seen, bromide recovery is high at both sampling points and all in situ hold times. In contrast, acetate recovery is initially high, but then declines with increasing in situ hold time at both the affected and unaffected sampling points. The decline with time at the unaffected point is likely the result of anaerobic degradation as the physical model was filled with water containing high sulfate concentrations (>100 mg/L). For short in situ hold times (<4 h), the loss due to degradation is so low that differences between affected and unaffected points are small. For longer in situ hold times (24 to 48 h), acetate loss is complete at both points. Thus, it appears that there is a window of in situ hold times for which the sensitivity of the technique is maximized. In these experiments, that window appears to be 12 to 24 h. It should be noted that the temperature of water in the physical model was high (27 to 33°C) relative to typical in situ conditions (15 to 20°C), and this might have induced higher acetate degradation rates than might occur in field settings.

As is evidenced in the results presented in Figure 2, the high Henry's Law Constant of SF_6 (>100 mg/L-vapor/mg/L-water) renders it difficult to use for this test. First, it requires the user to take special precautions when delivering and recovering solutions, since the SF_6 will completely partition into small volumes of gas. In this work, solutions were delivered from, and recovered into gas-tight Tedlar™ bags to eliminate gases prior to injection and to capture any gases pumped up to ground surface. The SF_6 also has a strong tendency to partition into trapped aquifer gases (Fry et al., 1995), which in turn, hinders its recovery and decreases the sensitivity of the volatilization rate measurement. To avoid this problem, it is recommended that practitioners use some other compound with a Henry's Law Constant in the range 0.1 to 1 mg/L-vapor/mg/L-water since this range of values is more representative of typical contaminants of interest, and compounds with these Henry's Law Constants are not expected to be significantly retained by trapped gas in the aquifer. At this time, however, it is not clear what the best options might be to

replace SF_6. Of course, this diagnostic test can be conducted without the volatile/non-degradable tracer; in that case the results can be used to assess aerobic biodegradation rates, but not volatilization rates.

6.0 FIELD APPLICATION OF THE DIAGNOSTIC TOOL

The push-pull diagnostic tool was field-tested at the Hydrocarbon National Test Site (HNTS) located at the U.S. Naval Construction Battalion Center in Port Hueneme, California. At the HNTS, groundwater has been impacted by a relatively large gasoline release from the Base service station. For this work, the push-pull test was applied to an IAS system installed within the areal extent of the residual immiscible hydrocarbon source zone. As this area was being used for other IAS research studies, there was an extensive monitoring network available and the site was already relatively well-characterized.

At the field test site, there are 12 multi-level monitoring installations, each containing a bundle of 15 1/8-inch color-coded, stainless steel sampling lines with ports at 2, 4, 6, 8, 10, 11, 12, 13, 14, 15, 16, 17, 18, and 19 ft below ground surface. The groundwater table is located at approximately 10 ft BGS, and the immiscible hydrocarbon smear zone extends from approximately 10 to 13 ft BGS. Dissolved total hydrocarbon concentrations in the smear zone generally exceeded 1 mg/L. A plan-view schematic diagram of the test site monitoring network is shown in Figure 3. For reference, MP1, MP2, and MP3 are located 5 ft from the IAS well; MP4, MP5, and MP6 are located 10 ft from the IAS well; MP7, MP8, and MP9 are located 20 ft from the IAS well; and MP10, MP11, and MP12 are located 30 ft from the IAS well. The IAS well was screened from 18 to 20 ft BGS. It is known from other studies at the HNTS IAS research site that the air distribution in the aquifer is non-uniform about the air injection well, exhibiting tendencies to flow in the general directions of MP6, MP12, MP3 and MP9.

The diagnostic test was applied at several monitoring locations while the IAS air injection flow rate was 20 standard cubic feet per minute (SCFM). Test locations within the target treatment zone were selected so that one to two locations from each radial distance away from the IAS well were used. All test points were located 11 ft BGS in the hydrocarbon smear zone. In each case the injected concentrations of bromide and acetate were approximately 50 mg/L, the injected volume was 1 L, extracted volumes were at least 4 L, and the in situ hold time was 25 h. The experimental procedure was as follows:

1. Preparation of 11 L of a solution containing approximately 50 mg/L each of bromide and acetate, and 2 mL of a 10% fluorescein solution.

2. De-oxygenation of this solution by N_2 gas bubbling.

3. Addition of ? ppm_v SF_6 to solution through gas bubbling and headspace recirculation.

4. Collection of groundwater samples from the test points for a background ion analysis and measurement of dissolved oxygen (DO). The preferred method is to pump slowly from the sampling point and to place the DO probe in a flow-through cell.

5. Collection of a 40 mL sample from the multi-tracer stock solution carboy for analysis of initial tracer concentrations.

6. Injection of 1-L of tracer solution into each test point with a peristaltic pump as quickly as the formation will allow.

7. Allowing the solution to remain in situ for 25 hours.

8. Extraction of 4 to 10 L of groundwater from each test point, along with measurement of DO; the visible dye is used as an indicator to judge how much groundwater to withdraw (in most cases only 4 to 5 L was necessary, but more was withdrawn in some instances).

9. Collection of 40 mL groundwater samples from each 1 L of extracted groundwater; this sample is saved on ice for tracer analysis. Generally, it is sufficient to collect a single sample from a well-mixed vessel containing all of the extracted groundwater; however, in this study we also wanted to assess how much mass was withdrawn in each 1-L increment.

10. Analysis of samples within 3 days of collection to ensure the validity of measured acetate levels; tests showed acetate concentration stability over approximately 7 d for samples stored on ice.

Results from the field test are presented in Table 1. In the data reduction, MP5 was taken to be the background point as the adjusted acetate and SF_6 recoveries were 94% and 81%, respectively, and other measurements at the site suggested that it was not within the area influenced by the air injection. As can be seen, the calculated oxygenation rates range from 7 to 51 mg-O_2/L-water/d. These can be converted to estimated potential aerobic biodegradation rates of approximately 2 to 17 mg-hydrocarbon/L-water/d. For reference, this range is also equivalent to a zero-order biodegradation rates of 0.4 to 3 mg-hydrocarbon/kg-soil/d, which is comparable to the lower end of the range of rates reported for bioventing in situ respirometry tests (Leeson and Hinchee, 1996).

The adjusted SF_6 recoveries in the field tests ranged from approximately 51% to 124%, and therefore were generally much greater than the recoveries in the laboratory-scale physical model development studies. The reason for this discrepancy is unknown, although it could be caused by differences in trapped gas concentrations in the two settings. The estimated volatilization rates shown in Table 2 range from 0 to 47%/d, with most values being at or near zero. There appears to be little

correlation between the estimated volatilization and oxygenation rates. This is unusual, as one would expect to see high oxygenation rates at locations having high volatilization rates. Again, this might be an artifact of the lack of sensitivity in the volatilization measurement suggested by the laboratory-scale development studies.

The results also show little correlation between dissolved oxygen concentrations and oxygen transfer rates at each test point. The data suggest that significant oxygen transfer occurs at points where DO measurements remain ≤1 mg/L. For this to happen, the rate of oxygen delivery is matched by the oxygen consumption rate at those points. This is an important finding as DO measurements are commonly used to define the zone of impact of an IAS system. The transfer of oxygen at points not showing elevated DO levels is also suggested in the IAS tracer gas delivery studies reported by Amerson (1997) and Bruce et al. (2000). To further illustrate this finding, Figure 4 presents the data appearing in Table 1 along with data collected from other push-pull diagnostic test applications at the HNTS IAS test site, for a range of IAS operating conditions. As can be seen, most of the oxygenation rates fall in the 0 to 50 mg-O_2/L-water/d range, although one value is as high as 100 mg-O_2/L-water/d. In general, this figure shows non-zero oxygenation rates at all points where elevated DO levels were observed; however, non-zero oxygenation rates were also observed at points showing no increase in dissolved oxygen.

In summary, a push-pull diagnostic test for IAS systems has been developed and tested. Oxygenation rates from the test site generally ranged from 5 to 40 mg-O_2/L-water/d, which corresponds to hydrocarbon conversion rates of approximately 1.7 to 13 mg-hydrocarbon/L-water/d and first-order aerobic biodegradation rates of approximately 0.3 to 2.4 mg-hydrocarbon/kg-soil/d. Significant oxygenation rates were observed at test points not exhibiting increased dissolved oxygen concentrations. It should be noted that the oxygenation and aerobic biodegradation rates obtained from this push-pull diagnostic test might be regarded as upper-bound estimates of actual aerobic biodegradation rates because: a) the tracer compound used here (acetate) is inherently more rapidly degraded than typical contaminants of interest (e.g., petroleum compounds), and b) it is assumed that all acetate loss above background levels is due to aerobic biodegradation and that complete mineralization occurs. The test might also underestimate oxygenation rates as other oxygen demands in the aquifer are neglected. In addition, it should be noted that there are situations for which this test might not be useful; these include: a) the formation does not accept the tracer solution, or does not allow recovery, in a reasonable amount of time, b) there are high background levels of acetate or fluoride, c) initial (pre-air sparging) groundwater DO > 5 mg-O_2/L-water, and d) the available monitoring point screen intervals or other well construction details cause impracticable volumes of tracer solution to be used (i.e. V_{well} is too large).

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Table 1. Sample data for field implementation of the push-pull diagnostic test (initial concentrations of bromide and acetate ions are 45.6±1.4 mg/L and 52.1±1.4 mg/L, respectively; in situ hold time is 25 h).

June-July 1997 Raw Data and Concentration Adjustments						
Monitoring Point	Cumulative Bromide Recovered (mg)	Fraction of Bromide Recovered (-)	Cumulative Acetate Recovered (mg)	Adjusted Acetate Recovered (mg)	Cumulative SF_6 Recovery (%)	Adjusted Cumulative SF_6 Recovery (%)
MP1-11	33.0	0.81	29.9	36.8	61.4	75.5
MP2-11	21.3	0.52	0.0	0	48.9	94.4
MP4-11	20.2	0.50	16.6	33.1	59.0	118
MP5-11	26.6	0.65	28.5	43.5	81.3	124
MP7-11	34.1	0.87	22.0	25.2	85.7	98.1
MP9-11	43.6	1.07	21.9	20.5	54.5	51.1
MP11-11	36.1	0.79	33.5	42.3	89.2	113

Data Reduction					
Monitoring Point	In Situ Hold Time (d)	DO (mg/L)	Oxygen Consumption Rate* (mg-O_2/L-water/d)	Aerobic Biodegradation Rate (mg-HC/L-water/d)	Volatilization Rate* (%/d)
MP1-11 (11 ft BGS)	1.04	<2	7.8	2.6	24
MP2-11 (11 ft BGS)	1.04	<2	51	17	5.4
MP4-11 (11 ft BGS)	1.04	4.5	12	3.9	0
MP5-11 (11 ft BGS)	1.04	<2	0	0	0
MP7-11 (11 ft BGS)	1.04	<2	20	6.7	1.8
MP9-11 (11 ft BGS)	1.04	6.1	27	9.0	47
MP11-11 (11 ft BGS)	1.04	<2	7.2	2.4	0

* - using the data from MP-5 as the background point